7489

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 754 748 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.01.1997 Bulletin 1997/04

(51) Int. Cl.[6]: **C11D 3/00**, C11D 3/37

(21) Application number: **95202004.8**

(22) Date of filing: **20.07.1995**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT SE

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(72) Inventor: **Fredj, Abdennaceur (NMN)**
B-1853 Strombeek-Bever (BE)

(74) Representative: **Canonici, Jean-Jacques et al**
Procter & Gamble European Technical Center N.V.
Temselaan 100
1853 Strombeek-Bever (BE)

(54) Detergent compositions inhibiting dye transfer

(57) A dye transfer inhibiting composition comprising a vinylpyridine wherein the molar ratio of copolymerizing monomer to vinylpyridine is from 1 to 0.01, preferably from 0.5 to 0.05, most preferably from 0.3 to 0.05.

EP 0 754 748 A1

Printed by Rank Xerox (UK) Business Services
2.13.13/3.4

Description

Field of the Invention

The present invention relates to a composition and a process for inhibiting dye transfer between fabrics during washing. More in particular, the present invention relates to detergent compositions comprising water-soluble vinylpyridine copolymers.

Background of the Invention

One of the most persistent and troublesome problems arising during modern fabric laundering operations is the tendency of some colored fabrics to release dye into the laundering solutions. The dye is then transferred onto other fabrics being washed therewith.

One way of overcoming this problem would be to complex or adsorb the fugitive dyes washed out of dyed fabrics before they have the opportunity to become attached to other articles in the wash.

Polymers have been used within detergent compositions to inhibit dye transfer. One type of such polymers are N-vinylimidazole homo-and copolymers. Examples of said polymers are described in prior art documents such as DE 2 814 287-A which relates to detergent compositions comprising 0.1 to 10 wt% water-soluble or water-dispersible N-vinyl imidazole homo- or copolymer in combination with anionic and/or nonionic surfactants and other detergent ingredients. EP 372 291 relates to a process for washing discolouration-sensitive textiles. The wash liquor contains anionic/nonionic surfactants and watersoluble polymers e.g. (co)polymers N-vinylimidazole, N-vinyloxazolidone or N-vinylpyrrolidone. EP 327 927 describes a granular detergent additive comprising water-soluble polymeric compounds based on N-vinylpyrrolidone and/or N-vinylimidazole and/or N-vinyloxazolidone and cationic compounds. DE 4027832-A discloses electrolyte-free liquid detergent compositions comprising zeolite A, nonionic surfactants and dye transfer inhibiting polymers. The dye transfer inhibiting polymers are homo-and copolymers selected from N-vinylpyrrolidone and/or N-vinylimidazole and/or N-vinyloxazolidone. Polyamine N-oxide are described in European Patent Application No. 93201198.4.

It has now been found that water-soluble vinylpyridine copolymers are very efficient in eliminating transfer of solubilized or suspended dyes.

This finding allows to formulate detergent compositions which exhibit excellent cleaning and dye transfer inhibiting properties.

According to another embodiment of this invention a process is also provided for laundering operations involving colored fabrics.

Summary of the invention

The present invention relates to dye transfer inhibiting compositions comprising a polymer selected from water-soluble vinylpyridine copolymers.

Detailed description of the invention

The vinylpyridine copolymer

The present invention comprises as an essential ingredient a polymer selected from the class of water-soluble vinylpyridine copolymers.

The vinylpyridine copolymers have an average molecular weight range from 5000-1,000,000.

Highly preferred polymers for use in the dye transfer inhibiting compositions according to the present invention comprise a polymer selected from vinylpyridine copolymers wherein said polymer has an average molecular weight range from 5,000 to 100,000 more preferably from 10,000 to 30,000, most preferably from 10,000 to 2O,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113. "Modern Methods of Polymer Characterization. In addition, it has been found that an excellent overall detergency performance of detergent compositions comprising vinylpyridine copolymers can be obtained by selecting a specific average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000. The vinylpyridine copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith. Any copolymerizing groups can be used as long as the polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable copolymerizing groups include formic acid, arylic acid, maleic acid, vinylpyrrolidone, vinyl acetate. Preferred copolymers are based on 4-vinylpyridine with vinylpyrrolidone, acrylic acid and maleic acid.

The vinylpyridine copolymerizing monomer of the present invention has a molar ratio of copolymer to vinylpyridine from 1 to 0.01, preferably from 0.5 to 0.05, most preferably from 0.3 to 0.05.

The vinylpyridine copolymers can be linear or branched. The vinylpyridine copolymers of the present invention are typically present from 0.001 to 10%, more preferably from 0.01 to 2%, most preferred from 0.05 to 1% by weight of the dye transfer inhibiting composition.

The present compositions are conventiently used as additives to conventional detergent compositions for use in laundry operations. The present invention also encompasses dye transfer inhibiting compositions which will contain detergent ingredients and thus serve as detergent compositions. The level of the vinylpyridine copolymer present in the detergent compositions is from 0.01 to 10%, more preferably from 0.05 to 5%, most preferably from 0.1 to 1% by weight of the detergent composition.

Method of making the vinylpyridine copolymer

The polymer is usually prepared by copolymerizing vinylpyridine with water soluble monomers in one or a mixture of water, methanol, isopropanol and acetone in the presence of polymerization initiator(s) such as water soluble azo initiators, sodium persulfate and/or hydrogen peroxide, and optionally a chain transfer agent. Typical reaction temperatures are 70-90°C and pH is 3-7.

DETERGENT ADJUNCTS

In another embodiment of the present invention, the detergent composition may comprise one or more of a surfactant selected from a wide range of surfactants.

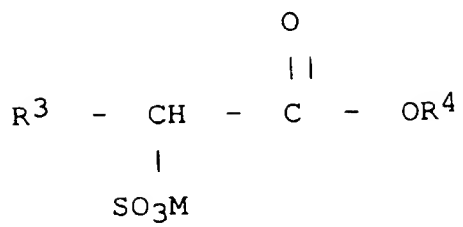
A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

Highly preferred anionic surfactants include the alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{18} alkyl component, more preferably a C_{12}-C_{15} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. monoethanolamine, methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Branched alkylsulfates are especially preferred.

Preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, more preferably C_{12}-C_{15} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation (e.g. monoethanolamine, methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{15} alkyl polyethoxylate (1.0) sulfate (C_{12}-$C_{15}E(1.0)M$), C_{12}-C_{15} alkyl polyethoxylate (2.25) sulfate (C_{12}-$C_{15}E(2.25)M$), C_{12}-C_{15} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{15}E(3.0)M$), and C_{12}-C_{15} alkyl polyethoxylate (4.0) sulfate (C_{12}-$C_{15}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Other suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

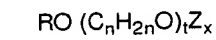
Other anionic surfactants useful for detersive purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulfonates, C_8-C_{22} primary of secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12}-C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6-C_{12} diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k$-CH_2COO-M+ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 5% to about 25% by weight of such anionic surfactants.

One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 14, more preferably from 12 to 14. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

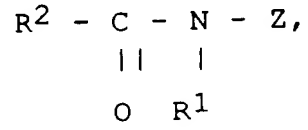
Especially preferred nonionic surfactants of this type are the C_9-C_{15} primary alcohol ethoxylates containing 3-12 moles of ethylene oxide per mole of alcohol, particularly the C_{12}-C_{15} primary alcohols containing 5-8 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

Highly preferred nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Other suitable nonionics are amine oxide surfactants. The compositions of the present invention may comprise amine oxide in accordance with the general formula I:

$$R^1(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2.qH_2O \qquad (I)$$

In general, it can be seen that the structure (I) provides one long-chain moiety $R^1(EO)_x(PO)_y(BO)_z$ and two short chain moieties, CH_2R'. R' is preferably selected from hydrogen, methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. When x+y+z = 0 , R^1 is a hydrocarbyl moiety having chainlength of from about 8 to about 18. When x+y+z is different from 0, R^1 may be somewhat longer, having a chainlength in the range C_{12}-C_{24}. The general formula also encompasses amine oxides wherein x+y+z = 0 , R_1 = C_8-C_{18}, R' = H and q = 0-2, preferably 2. These amine oxides are illustrated by C12-14 alkyldimethyl amine oxide,hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein x+y+z is different from zero, specifically x+y+z is from about 1 to about 10, R^1 is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments y + z is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Preferred embodiments include dodecyldimethylamine, tetradecyldimethylamineoxidedihydrate, hexadecyldimethylamin eoxidedihydrate and octadecyldimethylamine oxide dihydrate.

Whereas in certain of the preferred embodiments R' = H, there is some latitude with respect to having R' slightly larger than H. Specifically, the invention further encompasses embodiments wherein R' = CH_2OH, such as hexadecylbis(2- hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2- hydroxyethyl)amine oxide, dodecyldimethyl(2- hydroxyethyl)amine oxide dihydrate.

Other suitable nonionic surfactants comprises alkyl polyglucoside compounds of general formula

$$RO\ (C_nH_{2n}O)_tZ_x$$

wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

When included therein, the laundry detergent compositions of the present invention typically comprise nonionic surfactants in the weight ratio of anionic surfactant to nonionic surfactant from 6:1 to 1:3, preferably from 5:1 to 2:1.

Cationic detersive surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula :

$$[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N+X-$$

wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :

$$R_1R_2R_3R_4N^+X^- \qquad (i)$$

wherein R_1 is C_8-C_{16} alkyl, each of R_2, R_3 and R_4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and -

$(C_2H_4O)_xH$ where x has a value from 1 to 5, and X is an anion. Not more than one of R_2, R_3 or R_4 should be benzyl.

The preferred alkyl chain length for R_1 is C_{12}-C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
octyl or decyl triethyl ammonium chloride;
octyl or decyl dimethyl hydroxyethyl ammonium chloride or bromide;
C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
coconut dimethyl hydroxyethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl $(ethenoxy)_4$ ammonium chloride or bromide; choline esters (compounds of formula (i) wherein R_1 is - CH_2-O-C(O)-C_{12-14} alkyl and $R_2R_3R_4$ are methyl).

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0.5% to about 5%, preferably from about 1% to about 3% by weight of such cationic surfactants.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula R-CH(COOH)CH2(COOH) wherein R is C10-20 alkyl or alkenyl, preferably C12-16, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate , myristyl succinate, palmityl succinate2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid. Another preferred builder system for liquid compositions is based on dodecenyl succinic acid and citric acid.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Other detergent ingredients that can be included are detersive enzymes which can be included in the detergent formulations for a wide variety of purposes including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.05 mg to about 3 mg, of active enzyme per gram of the composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B.subtilis and B.licheniforms. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames Alcalase, Savinase and Esperase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands) and FN-base by Genencor, Optimase and opticlean by MKC.

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A is described in European Patent Application 130,756. Protease B is described in European Patent Application Serial No. 87303761.8. Amylases include, for example, - amylases obtained from a special strain of B.licheniformis, described in more detail in British Patent Specification No. 1,296,839 (Novo). Amylolytic proteins include, for example, Rapidase, Maxamyl (International Bio-Synthetics, Inc.) and Termamyl,(Novo Industries).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have

a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028 ; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800, and cellulases produced by a fungus of Bacillus N or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusc (Dolabella Auricula Solander). Other suitable cellulases are cellulases originated from Humicola Insulens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Such cellulase are described in Copending European patent application No. 93200811.3, filed March 19, 1993.

Especially suitable cellulase are the cellulase having color care benefits. Examples of such cellulases are cellulase described in European patent application No. 91202879.2, filed November 6, 1991 Carezyme (Novo).

In general, cellulases are preferred enzymes in that cellulases achieve a multicycle softening benefit, which is restricted to cotton containing fibers, by cleaving and assisting the removal of cellulosic fibrils. These normally form on the fibers during the normal washing process, and increase after consecutive washes and upon ageing of the fabric. The interaction of these fibrils with each other impart a degree of rigidity to the fabric surface that is felt by the consumer as harshness, which is alleviated by the use of cellulase enzymes.

The cellulases can be added in combination with softening silicones. Softening silicones deliver their single cycle softening benefit by depositing directly on the fabric.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunoligical cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P".
Especially suitable Lipase are lipase such as M1 Lipase (Ibis) and Lipolase (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes of pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro-and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT Internation Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.
In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. patent 4,318,818. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., such as diethanolamine, triethanolamine, diisopropanolamime, etc.), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. patent 4,261,868, U.S. Patent 3,600,319, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5. Non-boric acid and borate stabilizers are preferred. Borate may be conveniently incorporated into Heavy Duty Liquid detergent in the form of a solution. Boric acid has a solubility in water of about 13% at 60°C. Sodium metaborate is commercially available as a solution with activity of 10.1% (expressed in terms of B2O3) at 20°C.

For compact liquids it is preferred that the solution be concentrated. More concentrated solutions may be obtained by neutralising boric acid with organic amines, such as monoethanolamine (MEA).

A highly preferred concentrated borate solution can be prepared by heat treatment of aqueous borate solution. A solution heated to a temperature above 60°C, and preferably above 90°C, and maintained at that temperature for at least 5 minutes, preferably between 30 and 60 minutes will be stable at 20°C for at least a month. Using this heat treatment method, a solution with activity of at least 33% (expressed in terms of B2O3) can be made and stored without separation or precipitation.

Whilst various counterions may be used in the solution, e.g. sodium, potassium, MEA, triethanolamine etc, sodium is most preferred. The preferred molar ratio of Na2O: B2O3 is 0.15:1 to 0.38:1, more preferably 0.22:1 to 0.35:1.

Boric acid, metaborate or borax may all be used as raw materials. Other polyols such as glycerol may also be incorporated into the concentrated solution.

Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319 and 3,519,570.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent aplication N 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones

can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alcanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^{R}.

Other preferred suds controlling agents are described in EP 495 345. These suds controlling agents comprise a silicone antifoam compound, a carrier material and an organic coating material further containing glycerol at a weight ratio with the silicone antifoam compound of 1:2 to 3:1.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Other components used in detergent compositions may be employed, such as soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and non-encapsulated and encapsulated perfumes.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula

$$(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}[T\text{-}PO)_{2.8}(T\text{-}PEG)_{0.4}]T(PO\ H)_{0.25}((PEG)_{43}CH_3)_{0.75}$$

where PEG is $-(OC_2H_4)O-$, PO is (OC_3H_6O) and T is $(pcOC_6H_4CO)$.

Also very useful are modified polyesters as random copolymers of dimethyl terephtalate, dimethyl sulfoisophtalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephtalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoid acid and about 15% by weight of sulfoisophtalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

Preferred polymers for incorporation into the dye transfer inhibiting composition of the present invention include polyamine N-oxide polymers, copolymers of N-vinylpyrolidone and N-vinylimidazole, polyvinylpyrolidone, polyvinyloxazolidone and polyvinylimidazole. Said polymers are described in EP 622 447.

The detergent compositions according to the invention can be in liquid, paste, gels, bars or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher

density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water,compared to conventional liquid detergents. Typically, the water content of the concentrated liquid detergent is less than 30%, more preferably less than 20%, most preferably less than 10% by weight of the detergent compositions.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20 to 60, but the polymers are effective at up to 95°C and higher temperatures. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

The process and compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The following examples are meant to exemplify compositions of the présent invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

A liquid detergent composition according to the present invention is prepared, having the following compositions :

Table I

% by weight of the total detergent composition	
Fatty acid	10
Oleic acid	4
Citric acid	1
NaOH	3.4
Propanediol	1.5
Ethanol	10

EXAMPLE 1

The extent of dye transfer from different colored fabrics was studied using a launder-o-meter test that simulates a 30 min wash cycle. The launder-o-meter beaker contains 200 ml of a detergent solution, a 10cmx10cm piece of the colored fabric and a multifiber swatch which is used as a pick-up tracer for the bleeding dye. The multifiber swatch consists of 6 pieces (1.5cmx5cm each) of different material (polyacetate, cotton, polyamide, polyester, wool and orlon) which are sewn together.

The extent of dye transfer is assessed by a Hunter Colour measurement. The Hunter Colour system evaluates the colour of a fabric sample in terms of the DE value which represents the change in the Hunter L, a, *b*, values which are determined by reflecting spectrometrie. The ΔE value is defined by the following equation:

$$\Delta E = \{(a_f - a_i)^2 + (b_f - b_i)^2 + (L_f - L_i)^2\}^{1/2}$$

where the subscripts i and f refer to the Hunter value before and after washing in the presence of the bleeding fabric, respectively. The least significant difference is 1 at 95% confidence level.

Example I demonstrates the enhanced dye transfer inhibiting performance of the vinylpyridine copolymers.

Experimental conditions

30°C/city water

A : a detergent composition according to Table I which does not contain any dye transfer inhibition system.

B : a detergent composition according to Table I containing poly(4-vinylpyridine)-co-(acrylate) with a 4-vinylpyridine/acrylate ratio of 85/15. The level of copolymer in solution is 7ppm.

Results :

ΔE values for cotton

DYE	A	B
Direct black 112	13.1	3.6
Direct violet 47	15.1	7.1

EXAMPLE II (A/B/C)

A liquid detergent composition according to the present invention is prepared, having the following compositions :

% by weight of the total detergent composition			
	A	B	C
Linear alkylbenzene sulfonate	10	-	-
Alkyl alkoxylated sulfate	-	9	-
Polyhydroxy fatty acid	-	-	9
Trimethyl ammonium chloride C12-C14	-	-	4
Alkyl sulphate	4	4	4
Fatty alcohol (C_{12}-C_{15}) ethoxylate	12	12	12
Fatty acid	10	10	10
Oleic acid	4	4	4
Citric acid	1	1	1
Diethylenetriaminepentamethylene Phosphonic acid	1.5	1.5	1.5
NaOH	3.4	3.4	3.4
Propanediol	1.5	1.5	1.5
Ethanol	10	10	10
Ethoxylated tetraethylene pentamine	0.7	0.7	0.7
Poly(4-vinylpyridine)-co-(acrylate)	0-1	0-1	0-1
Thermamyl	0.13	0.13	0.13
Carezyme	0.014	0.014	0.014
FN-Base	1.8	1.8	1.8
Lipolase	0.14	0.14	0.14
Endoglucanase A	0.53	0.53	0.53
Suds supressor (ISOFOL[r])	2.5	2.5	2.5
Minors	up to 100		

EXAMPLE III (A/B/C)

A compact granular detergent composition according to the present invention is prepared, having the following formulation:

% by weight of the total detergent composition			
	A	B	C
Linear alkyl benzene sulphonate	11.40	-	-
Alkyl alkoxylated sulfate	-	10	-
Polyhydroxy fatty acid	-	-	9
Trimethyl ammonium chloride C12-C14	-	-	4
Tallow alkyl sulphate	1.80	1.80	1.80
C_{45} alkyl sulphate	3.00	3.00	3.00
C_{45} alcohol 7 times ethoxylated	4.00	4.00	4.00
Tallow alcohol 11 times ethoxylated	1.80	1.80	1.80
Dispersant	0.07	0.07	0.07
Silicone fluid	0.80	0.80	0.80
Trisodium citrate	14.00	14.00	14.00
Citric acid	3.00	3.00	3.00
Zeolite	32.50	32.50	32.50
Maleic acid actylic acid copolymer	5.00	5.00	5.00
Cellulase (active protein)	0.03	0.03	0.03
Alkalase/BAN	0.60	0.60	0.60
Lipase	0.36	0.36	0.36
Sodium silicate	2.00	2.00	2.00
Sodium sulphate	3.50	3.50	3.50
Poly(4-vinylpyridine)-co-(acrylate)	0-1	0-1	0-1
Minors	up to 100		

The above compositions (Example II(A/B/C) and III(A/B/C)) were very good at displaying excellent clay and detergent performance with outstanding color-care performance on colored fabrics and mixed loads of colored and white fabrics.

Claims

1. A dye transfer inhibiting composition comprising a vinylpyridine copolymer.

2. A dye transfer inhibiting composition according to claim 1 wherein the molar ratio of copolymerizing monomer to vinylpyridine is from 1 to 0.01, preferably from 0.5 to 0.05, most preferably from 0.3 to 0.05.

3. A dye transfer inhibiting composition according to claim 1 and 2 wherein the copolymer is selected from formic acid, acrylic acid, maleic acid, vinylpyrolidone and vinylacetate.

4. A dye transfer inhibiting composition according to claim 1-7 wherein the average molecular weight ranges from 5000 to 100 000, preferably from 5 000 to 100 000.

5. A detergent composition according to claims 1-3 wherein the average molecular weight of the vinylpyridine copolymer is from 5 000 to 50 000.

6. A detergent composition comprising the dye transfer inhibiting composition according to claims 1-5 further comprising a nonionic surfactant.

7. A detergent composition according to claims 5-6 further comprising polyamine N-oxide polymers, copolymers of N-vinylpyrolidone and N-vinylimidazole, polyvinylpyrolidone, polyvinyloxazolidone and polyvinylimidazole.

8. A detergent composition according to claims 5-7 which is in the form of a granular, liquid gel, paste or bar.

9. A dye transfer inhibiting composition according to claim 1-4 which is a detergent additive in the form of a non-dusting granule or a liquid.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2004

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO-A-94 11482 (PROCTER & GAMBLE CO.) * page 23, line 16 - line 17 *	1	C11D3/00 C11D3/37
A D	EP-A-0 579 295 (PROCTER & GAMBLE CO.) * Abstract * & EP-A-0 622 447	1	
A	EP-A-0 663 438 (PROCTER & GAMBLE CO.) * claims *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	17 January 1996	Pelli Wablat, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)